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CHARACTERIZATION OF III-V COMPOUND SEMICONDUCTOR DEVICE MATERIA—ETC(U)
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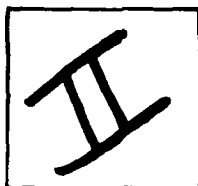


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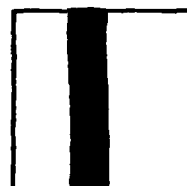
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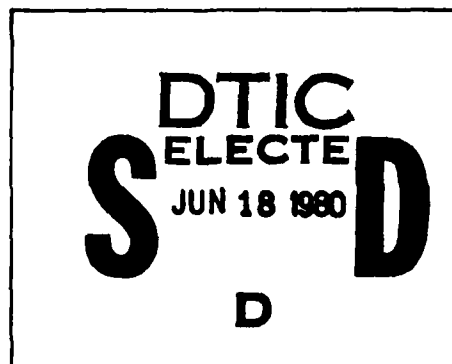
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CHARACTERIZATION OF III-V COMPOUND SEMICONDUCTOR
DEVICE MATERIALS

Electronic Research Branch
Electronic Technology Division

February 1980

TECHNICAL REPORT AFWAL-TR-80-1016

Final Report for Period July 1975 - October 1979

Approved for public release; distribution unlimited.

AIR FORCE AVIONICS LABORATORY
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FOR THE COMMANDER



PHILIP E. STOVER, Chief
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energy of excitons to foreign impurities and the energies of complexes were established. Transport measurements were used to measure carrier mobilities and electrical conductivity as well as carrier concentrations. These measurements as a function of temperature make it possible to determine the number of donors (N_D) and the number of acceptors (N_A) and therefore the compensation ratio in the material. Local vibrational mode spectroscopy was used as a characterization tool to identify specific impurities such as C and Si in GaAs. From the vibrational energy the site location of the impurity can be determined. These characterization techniques have been very successful in evaluating the quality of materials and have been very helpful to the crystal growing program which has been successful in growing very high quality materials.

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FOREWORD

This report covers the work performed under Task No. 2306R108, from July 1, 1975 to October 1, 1979. The objective of this task is to completely characterize the electronic impurity and defect structure of III-V semiconductors, including selected ternary and quaternary compounds. Emphasis is given to characterization of residual impurities, native defects, impurity dopants and concentration profiles in high purity and doped epitaxial layers and melt-grown substrate crystals. The homogeneity of impurities and lattice imperfections as well as the electronic defect structure at surfaces and interfaces of these materials is also investigated. A major part of the effort is devoted to impurity and defect characterizations in GaAs and In P materials required for high frequency microwave and opto-electronic devices such as diodes, power sources, high power FET's, digital processing systems, laser diodes, optical light guides and infrared detectors.

The principal contributors to the task effort during its existence were the following:

Maj Robert Almassy, Task Manager for part of the duration of the task.

C. W. Litton, Research Scientist

D. C. Reynolds, Current Task Manager

Most of the research has been reported in a series of papers published in the scientific literature, these are referenced at the end of each section.

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SECTION I

CHARACTERIZATION OF III-V COMPOUND SEMICONDUCTOR DEVICE MATERIALS

1. INTRODUCTION

The primary objective of this task has been the electrical, optical and magneto-optical characterization of the intrinsic and extrinsic properties of compound semiconductors, primarily from the III-V group of materials.

It has been demonstrated that the key to device development is the material from which the device is fabricated. In the interest of performance reliability and reproducibility it is desirable to develop the materials technology base that is required for a sound device technology. This requires a basic understanding of the material including the effects of foreign impurities, host defects and complexes involving both impurities and defects. Native defects can interact with intentionally introduced dopants to form neutral centers. In this case there would result a lack of one to one correspondence between added donors, for example, and free electron concentrations as determined from electrical measurements. This lack of one to one correspondence in GaAs has been explained by Schottky (Reference 1), Casey et al. (Reference 2), and Panish (Reference 3) as due to native defects compensating intentionally added impurities. It is also possible for residual acceptor impurities to compensate intentionally added donor impurities. In this case the donors will be ionized, as a result they cannot be detected by electrical measurements. However, as ionized centers they may bind excitons which can then identify these centers as ionized centers. This demonstrates how photoluminescent transitions resulting from exciton complexes can complement electrical measurements for materials characterization and the added dimension that it adds in identifying the nature of impurity or defect centers in semiconductors.

The effective mass like donors in III-V binary and in several of the III-V ternary systems are shallow. The chemical shifts and central cell corrections are small, therefore the energy separation of donors resulting

from different impurities or host defects is small. This requires low residual concentrations to prevent concentration broadening and merging of the impurity levels with the conduction band. Controlled doping experiments with known donors must also be in the low concentration range ($N_D < 5 \times 10^{14} \text{ cm}^{-3}$) to permit identification of specific donors. The concentration of host lattice defects must also be in this low concentration range since they may also create donor centers or complexes.

The binding energies of acceptors are in general larger than donors. This makes the experimental characterization of acceptors easier than that for donors.

Once the residual impurities and defects are controlled at an acceptable low level to permit effective controlled doping, dopants can be added to the growing system to obtain uncompensated, and uniformly doped material. In the growth of epitaxial layers the growth rate and the diffusion coefficient of the dopant will determine whether the impurity is incorporated into the growing layer in an equilibrium manner (the incorporation is controlled by the intrinsic carriers at the growth temperature) or in a non equilibrium manner (the incorporation is controlled by surface states) (References 4 - 6).

Sophisticated characterization capabilities are essential in order to satisfactorily analyze these high purity materials. An example of the precision required is the energy separation of effective mass like donors in GaAs. Four different donors have been observed in GaAs in an energy spread of less than 2cm^{-1} .

The importance of material properties to the quality of device performance has been well recognized. The investigation of the residual impurities, dopants, and lattice defects in high purity materials and the determination of how they interact and how they are incorporated into the lattice is part of the characterization procedure. These material parameters are then correlated with device properties - both performance and reliability. It is instrumental in providing material of greater uniformity, higher yields and lower costs. It will also allow the device manufacturer to select material with required properties prior to device

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fabrication. This is based on close coordination between crystal growth, and crystal characterization.

It is the goal of any material program to be able to control growth parameters to the degree necessary to tailor material properties for maximum device yield, performance, and reliability. This requires a complete understanding of the detailed nature of defects, impurities, and their interactions as well as uniformity of incorporation and position in the host lattice.

SECTION II

HIGH RESOLUTION OPTICAL AND MAGNETO-OPTICAL CHARACTERIZATION

Intense photoluminescence is observed in many semiconductors at low temperatures. When spectrally analyzed, this photoluminescence provides an extensive source of experimental data which contributes to the ultimate identification of the electronic states of impurities and defects in these semiconductors. Many sharp lines appear in such spectra, particularly from bound excitons, which provide a "finger print", of the impurities and defects which are present in the semiconductor lattice.

The exciton is the probe in this case, becoming bound to various impurities, defects, and complexes and the subsequent decay from the bound state yields information concerning the center to which it was bound. Early photoluminescent investigations were primarily centered on free to bound and bound to bound transitions such as the so called "edge emission" studies which gave rise to relatively broad emission. In the 1960's the effort shifted to more intensive studies of the sharp-line emission, aimed at identifying the bound exciton impurity transitions and at achieving a better understanding of the residual impurity and defect structure of semiconductors which have application in the electronic industry. The magnetic field splittings of these sharp line transitions make it possible to differentiate between neutral and ionized donor and acceptor impurities. In conjunction with systematic impurity doping experiments, specific donor and acceptor impurities may be identified.

It is also possible to differentiate between simple substitutional donors and acceptors and complexes composed of combinations of impurities and or defects.

1. EXPERIMENTAL TECHNIQUES IMPORTANT TO OPTICAL CHARACTERIZATION

The electrical properties of semiconductors has a long history of extensive investigation. Many of the basic properties of these materials were determined from electrical measurements. As the investigations of semiconductors were extended to some of the larger band gap materials

Electrical measurements were not as readily applicable. This coupled with the understanding of excitons and their contribution to the elucidation of material properties in the 1960's lead to a wide application of optical studies to semiconductor materials. It was found that these materials reflect, absorb, disperse, scatter and radiate light and in general interact strongly with the electromagnetic radiation field. Because of this strong interaction many of the fundamental properties of these materials such as their energy band gaps, activation energies of defects and foreign impurities, effective mass parameters, refractive indices, dielectric functions, exciton binding energies and lattice vibration frequencies can be determined from optical experiments. These experiments cover the electromagnetic spectrum, ranging from the vacuum ultraviolet to the far infrared. Over the past two decades, optical spectroscopy has been increasingly employed for the study and measurement of semiconductor properties and has ultimately become a very powerful experimental tool.

The technique of high resolution optical absorption, reflection and photoluminescence spectroscopy has been extensively used to analyze the intrinsic energy band parameters of semiconductors, as well as their impurity and defect states. Intrinsic or free exciton formation is observed in most well formed crystal structures when optically excited with the proper energy and at cryogenic temperatures. The free excitons have been applied with a great deal of success in probing the intrinsic band structure of semiconductors. Bound excitons have been applied equally successfully in probing the impurity and defect structure of many of these same materials.

With the advent of the laser as an exciting source optical studies have become even more rewarding, particularly so, when non linear effects are being investigated. They are also invaluable as exciting sources for high resolution photoluminescence studies. An experimental set up for high resolution spectroscopy is shown in Figures 1a, b and c). In these experiments the sample is mounted in a Dewar, the Dewar may be attached to a pumping system where temperatures near 1°K can be realized. The Dewar may also be placed between the poles of a magnet permitting magneto

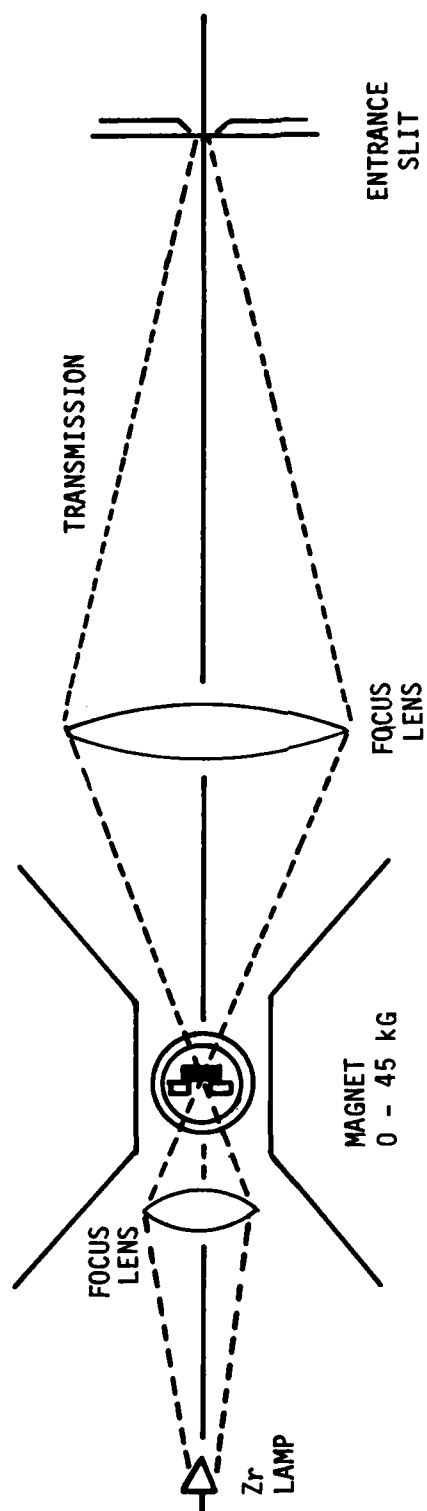


Figure 1a. Experimental Arrangement for Optical Transmission Measurements

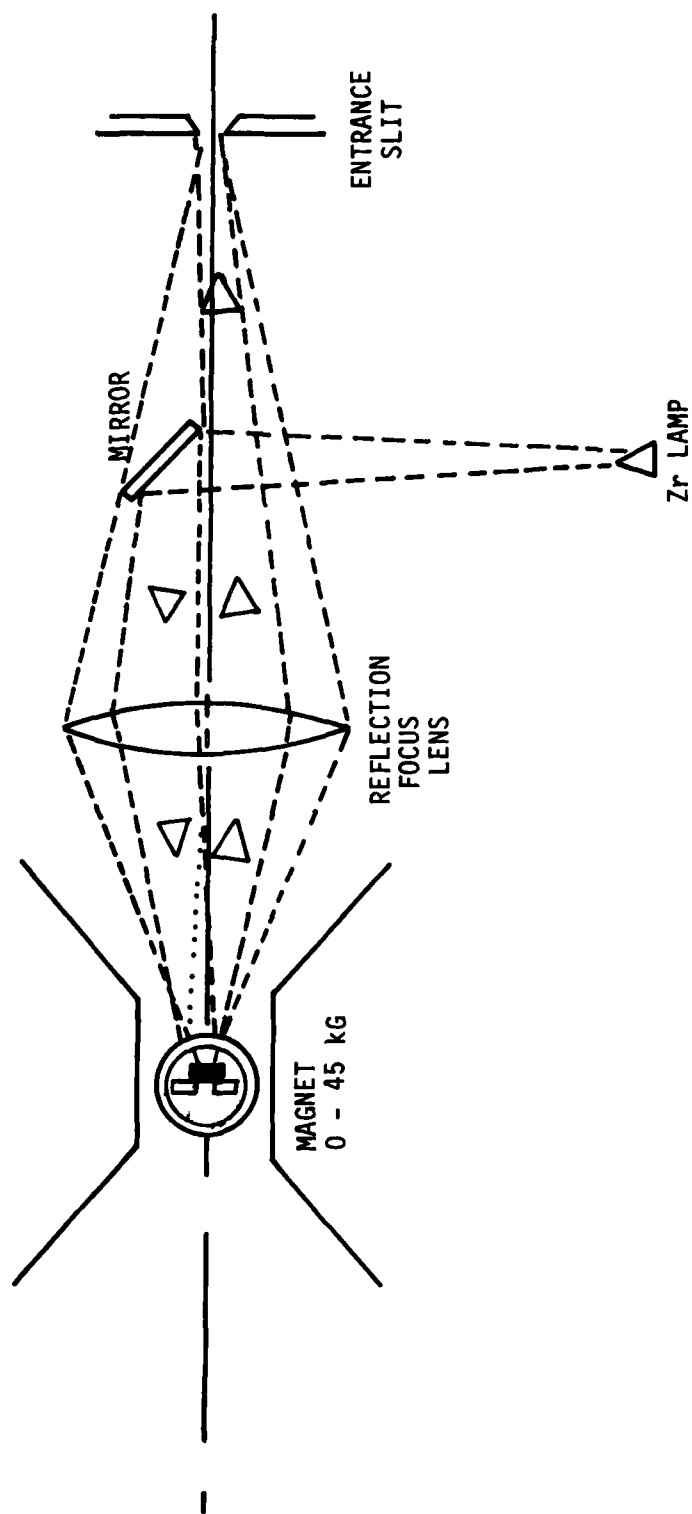


Figure 1b. Experimental Arrangement for Reflection Measurements

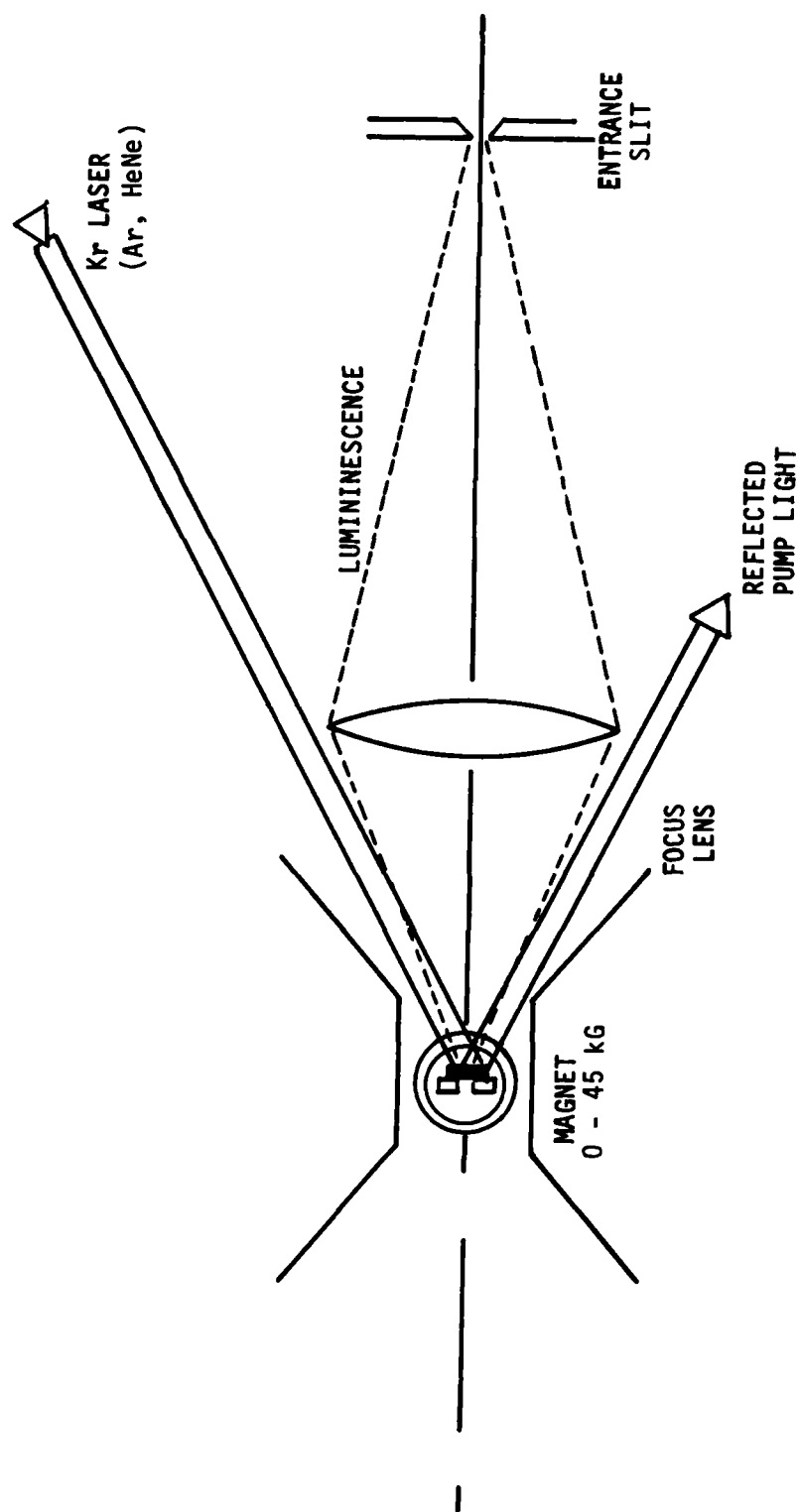


Figure 1c. Experimental Arrangement for Luminescence Measurements

optical studies to be made. The optical source is selected to be optimum for the specific material being investigated. The transmitted, reflected, or emitted light may then be analyzed with a high resolution spectrograph. The heart of the spectrograph is the grating which again will be selected to give optimum data for the particular material under investigation. An example of specific design parameters for such a spectrograph optimized for investigating GaAs will be given here. A spectrograph with a four meter focal length and an Ebert mount provides the housing for the optics. A 4 x 4 inch grating with 2160 grooves/mm and blazed at a 32° angle is the key to the optical performance. This design gives a dispersion of approximately 0.54Å/mm in first order in the free exciton spectral region of GaAs. Theoretical spectral energy resolution of 7×10^{-6} eV is achievable with this instrument. It may be designed with either photographic recording or electronic recording of the optical data.

Optical absorption coefficients in the free exciton region of semiconductor crystals are very large, particularly so for direct band gap materials. To obtain meaningful data very thin specimens are required.

Materials that crystallize in platelet form are particularly suited for absorption measurements in the free exciton region. Crystals having the wurtzite structure readily form platelet type structures. Platelets as thin as 0.2μ can be grown with sufficient areas to perform absorption measurements. The free exciton structure is readily discerned by this technique from which many of the material parameters can be deduced.

2. DIRECT OPTICAL TRANSITIONS

The quantum mechanical selection rules for optical transitions state that if κ_i and κ_f are the wave vectors for the electron in the initial and final state and if q is the wave vector of the radiation then $\kappa_f - \kappa_i = q$. For the case of optical transitions involving most materials in which excitons dominate, the wave vector of the electron is much larger than the wave vector of the photon. The selection rule then states that $\kappa_f = \kappa_i$. Transitions are only allowed in this case between a given band of specific wave vector to a higher band of the same wave vector. Materials having the minimum in the conduction band and the

maximum in the valence band at the same place in κ space are known as direct gap materials. The transitions in these materials are direct transitions, sometimes called vertical transitions.

The intensity of the absorption due to a direct transition depends on the density of occupied states in the valence band and on the density of empty states in the conduction band as well as the transition probability.

The absorption coefficient, neglecting electron-hole interaction, given by Fan (Reference 7) for this type of transition is:

$$\alpha = \frac{\pi e^2}{nm} f_{if} N(E) \quad (1)$$

f_{if} is the oscillator strength for the transition and is given by

$$f_{if} = \frac{2}{3m\hbar\nu} (M)^2 \quad (2)$$

$N(E)$ is the density of states function and M is the matrix element for the transition

$$M = \int \psi_f^* H_{int} \psi_i d\tau \quad (3)$$

Where H_{int} is the dipole moment operator for dipole transitions.

If spherical bands are assumed then the curvature of the bands are measures of the effective masses of the carriers, m_e and m_h . Using the definition for the effective masses one obtains

$$E - E_g = \hbar^2 k^2 / 2m_e + \hbar^2 k^2 / 2m_h \quad (4)$$

and the density of states in κ space is

$$dn/d\kappa = 8\pi\kappa^2 \quad (5)$$

The density of states function as a function of energy becomes

$$\frac{dN(E)}{dE} = \frac{8\pi}{h^3} [2 \mu^3 (E-E_g)]^{1/2} \quad (6)$$

where the reduced mass $\mu = m_e m_h / (m_e + m_h)$. For direct transitions the absorption coefficient in the vicinity of the absorption edge will depend primarily on $(h\nu - E_g)^{1/2}$, where ν is the frequency of the radiation and E_g is the energy gap. Brooks (Reference 8) has given the magnitude of the absorption coefficient as follows:

$$\alpha = \frac{e^2 (2\mu)^{3/2}}{\pi n C m_e h^2} f_{if} (h\nu - E_g)^{1/2} \quad (7)$$

Similar frequency dependencies of the absorption coefficient were given by Dexter (Reference 9).

3. INDIRECT OPTICAL TRANSITIONS

The indirect band to band absorption process requires the creation or annihilation of phonons to conserve momentum. The empty conduction band and filled valence band constitute the initial state. Absorption of a photon and phonon lead to the final state consisting of a hole with $\kappa_h = 0$ and an electron with $\kappa_c = \kappa_e$. The electron hole interaction is neglected when the absorption is described in terms of the one-particle states. The expression for the absorption coefficient for indirect transitions was given by Bardeen et al. (Reference 10) as follows:

$$\alpha = \frac{2e^2 (2m_r)^{5/2} (h\nu - E_g)^{3/2}}{3n c \hbar^2 m_T^2 h\nu} \quad (8)$$

Where m_T is the effective mass for the transition.

The creation of excitons by the indirect absorption process is discussed by Elliott (Reference 11). In this case the electron-hole interaction is included and a more complete description in terms of exciton states is obtained. For a detailed description of the absorption process see Knox (Reference 12).

4. TRANSMISSION EXPERIMENTS

In transmission measurements the radiation is attenuated by absorption and by reflection at the crystal surfaces. The technique usually employed is normal incidence on a crystal having parallel faces as shown in Figure 1a. The incident source is usually a white light source. The transmitted beam contains multiply reflected components. If interference effects are not included the transmittance T , as given by McMahan (Reference 13) is as follows:

$$T = \frac{(1-R)^2 e^{-\alpha d}}{(1-R^2 e^{-2\alpha d})} \quad (9)$$

where α is the absorption coefficient, d is the sample thickness and R is the reflectance at normal incidence at an air-sample interface. R is expressed in terms of the refractive index n and the extinction coefficient, K , ($K = \alpha\lambda/4\pi$) as follows:

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \quad (10)$$

It was shown by Stern that Equation 10 follows from solutions to Maxwells' equations from which the Fresnel formula for the reflection coefficient, r , is obtained. At normal incidence r , is given

$$r = R^{1/2} e^{i\theta} = (1-n-iK)/(1+n+iK) \quad (11)$$

In the above expression θ is the phase difference between the incident and reflected waves. When the optical properties are expressed in terms of the complex dielectric constant, $K = K_1 + iK_2$, K is related to n and K in the following way:

$$K_1 + iK_2 = (n + iK)^2 = n^2 - K^2 + i 2nK \quad (12)$$

At this point it is interesting to examine some of the real situations encountered in materials investigations. Some of the wide band gap compounds are representative examples. The spectral region of importance is approximately $5,000\text{\AA}$, $\alpha \sim 10^5 \text{ cm}^{-1}$ and $n \approx 3$. Considering $T \sim 10^{-4}$ as a practical lower limit, it is seen from Equation 9 that the

sample thickness for useful transmission measurements should not exceed $d \approx 10^{-4}$ cm. Sample thicknesses of this order can be obtained from evaporated layers however, these layers in general are polycrystalline. Platelet type samples of wurtzite materials are ideal for transmission measurements since they can be grown with high quality single crystal structure and in thicknesses as small as $d = 2 \times 10^{-5}$ cm. Platelets have not been grown from zinc-blende structures in either II-VI or III-V compounds. In view of this limitation thin specimens (of the order of 10^{-4} cm in thickness) cannot be grown.

Specimens may be prepared by polishing and etching however thickness irregularities plague this technique. Surface damage is also a problem in thinning samples by this technique.

5. REFLECTION SPECTRA

In dealing with materials that cannot be grown in thicknesses appropriate for useful transmission measurements, reflection measurements as shown in Figure 1b can be substituted. Consider the same parameters as above, $\lambda \approx 5000 \text{ \AA}$, $\alpha \approx 10^5 \text{ cm}^{-1}$ and $n \approx 3$. These values result in $K \approx 0.5$. R is therefore dominated by n rather than α except in the region of direct exciton absorption where α reaches values of 5×10^5 to 10^6 . The spectral variation of R is smaller than that of α , reflectivity measurements may however be used to obtain α . The phase angle between the incident and reflected radiation waves is related to the reflectivity as shown in Equation 11.

The phase angle is also related to the reflectivity by one of the Kramers-Kronig relations.

$$(\omega P) = \frac{\omega P}{\pi} \int_0^{\infty} \frac{\log R(\omega P) / \log R(\omega) d\omega}{\omega^2 - \omega P^2} \quad (13)$$

Where ωP is a given frequency point on the reflectivity curve, over which the integral is to be evaluated from $\omega=0$ to $\omega \rightarrow \infty$. Equating the real and imaginary parts of Equation 11 gives the expression for the optical constants, n and K , in terms of $R(\omega)$ and $\theta(\omega)$

$$K(\omega) = \frac{2R^{1/2} \sin \theta}{1+R-2R^{1/2} \cos \theta} \quad (14)$$

$$n(\omega) = \frac{1-R}{1+R-2R^{1/2} \cos \theta} \quad (15)$$

Equation 11 is summed numerically to obtain values of $\theta(\omega_p)$ at each frequency point of the experimentally measured reflectivity, $R(\omega)$. From Equations 14 and 15 and the known values of $R(\omega)$ and (ω) the imaginary part of the dielectric function ($2nK$) as a function of frequency (ω) can be calculated.

The absorption coefficient of an optically transparent medium is defined by the condition that the energy in the incident wave fall to $1/e$ of its initial value in a distance $\frac{1}{\alpha}$, and is given by

$$\alpha = 2\omega K/C = 4\pi K/\lambda \quad (16)$$

From Equation 16 and the known values of n and K , the absorption coefficient (α) as a function of frequency (ω) can be calculated. In this way the absorption spectrum of the semiconductor can be calculated from its reflection spectrum, and hence the resonant frequencies of the exciton transitions can be obtained.

6. PHOTOLUMINESCENCE SPECTRA

The photoluminescence process in the intrinsic region is difficult to quantitatively analyze. In the case of absorption and reflection experiments broad band illumination is used generally at relatively low intensities. This maintains the crystal in thermal equilibrium.

The complications in the theory result from uncertainty in the proper model for the dielectric function and the proper surface boundary conditions. These same problems are present in the photoluminescent process

with a number of additional problems. Exciting intensities are usually greater in the case of photoluminescence studies, laser excitation, is most generally used as shown in Figure 1c, as a result the crystal is not in thermal equilibrium.

Surface recombination as well as bulk and surface scattering have great influence on the photoluminescent results and for the most part are not quantitatively known. The interpretation of intrinsic photoluminescent spectra is in need of quantitative theory to yield as much reliable fundamental information as is obtained from absorption and reflection spectra.

7. SUMMARY OF RESULTS OBTAINED FROM HIGH RESOLUTION MAGNETO-OPTICAL SPECTROSCOPY

A number of the basic properties of GaAs and InP were determined from the intrinsic free exciton spectra of these materials. Among the properties determined were the exciton binding energy, the exchange energy, the band gap energy, effective mass of the electron, effective mass of the exciton, effective g-value of the electron and the effective κ -value of the hole. From the extrinsic exciton spectra (bound exciton) a number of impurities were identified along with their binding energies. A total of six complexes were observed for the first time and a model proposed to explain their composition.

A series of sharp lines were observed on the low energy side of the acceptor bound exciton at liquid helium temperature. These lines result from the radiative recombination of an exciton in a multi-exciton complex bound to a neutral acceptor. This marked the first observation of multi-bound excitons in a direct gap material. It is important to identify such transitions since it rules out additional impurities or defects in the material as contributing to these lines.

The results of high resolution optical and magneto-optical characterization on this task are described in the following journal articles:

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SECTION III

TRANSPORT MEASUREMENTS

1. INTRODUCTION

The doping of GaAs with Cr and/or O produces very high resistivity ($10^8 - 10^9 \Omega\text{-cm}$) material (Reference 15) which is extensively used to provide substrates for GaAs field effect transistors (FET), integrated circuits, and optoelectronic devices. However, thin-layer devices, such as high frequency FET's, can be strongly influenced by the interface region between the substrate and active layer (Reference 16). Therefore, substrate quality becomes important. Nearly everyone agrees, and indeed it has been experimentally shown, that substrate quality is one of the most important factors in the performance, reliability, and yield of GaAs FET's (Reference 17). For this reason, considerable effort has been devoted toward the solution of this problem.

2. ELECTRICAL MEASUREMENTS

In the area of electrical measurements, an automated high-resistivity Hall-effect and photoelectronic apparatus was designed and constructed which has state-of-the-art capabilities. Temperature can be automatically varied between 4.2 and 800°K; magnetic field, 0-19 kG; monochromatic light irradiation, irradiation with continuous source, spectral range 0.6-3.4 μm ; and light intensity, $0 - 3 \times 10^{15}$ photons/ cm^2sec over most of this wavelength range can be provided. The mixed-conductivity nature of semi-insulating GaAs can be taken into account automatically by use of a somewhat complex magnetic-field sequencing scheme (Reference 18). With this apparatus GaAs:Cr and GaAs:O has been extensively studied by the dark Hall, photo-Hall, photoconductivity, and photomagnetoelectric (PME) methods (Reference 19). The PME effect was investigated in the impurity (below band gap) regime for the first time and extended the PME theory to this regime (Reference 20). The usefulness of each of these techniques for "fingerprinting" the substrate materials was determined (Reference 15). Certain of the measured parameters were found to correlate, although weakly, with the "conversion propensity," i.e., the tendency of the sample to form a thin, conducting layer during high-temperature processing.

Furthermore, a correlation was found between the Cr concentration, as measured by spark-source mass spectroscopy (SSMS), and the Hall mobility (Reference 21). Unfortunately, commercially available SSMS results are unreliable in the 1 ppmA and below region especially for C and O, two of the most important impurities in GaAs. This is one problem that requires further work.

3. GaAs BUFFER LAYERS

One proposal to solve the substrate-active-layer interface problem involves growing a high-purity "buffer" layer between the two layers (Reference 16). This solution raises costs, of course, but may be necessary for adequate performance, reliability, and yield of the resulting devices. Measurements have been made on VPE layers grown, in the laboratory, with resistivities greater than $10^5 \Omega\text{-cm}$, qualifying them as "semi-insulating" substrates for many applications. It has been found that the epilayers of such resistivity are always controlled by a level 0.50 ± 0.02 eV above the valence band (Reference 22). Since Cr is often found in these epilayers, it is tempting to suggest that this center is Cr related. It could also, of course, be associated with a native defect, or both. In fact, this same level is seen in samples converted from n-type to p-type by irradiation (Reference 23) which supports the native-defect theory. The whole subject of native defects is extremely important.

4. NATIVE DEFECTS IN GaAs

The laboratory has a 1 MeV Van de Graaff accelerator which is very useful for creating point defects. Such simple defects, Ga and As vacancies and interstitials, must be understood before the more complex defects produced during growth, annealing, or ion implantation can be dealt with. Thus, a research effort has been devoted to this end and some results have already been realized. For example, levels at 0.1, 0.2, and 0.3 eV below the conduction band (Reference 24) and at 0.1 and 0.5 eV above the valence band (Reference 23), have been identified. Some of these levels correspond to those seen by deep level transient spectroscopy (DLTS) (Reference 25). Furthermore, for the first time, good

p-type GaAs has been produced from good n-type VPE layers. This process has technological possibilities and the results should be studied further. Also the ability to vary the Fermi level from near the conduction band to near the valence band, by electron irradiation, makes it possible, for the first time, to study levels throughout the whole band gap in the same sample.

5. IMPURITIES IN GaAs

Although impurities in connection with GaAs substrate and epilayer research have already been discussed, the subject deserves special mention because of the vast importance of impurities in nearly every phase of semiconductor device operation. Semiconductor researchers must be able to obtain accurate impurity analyses of elements like Cr, O, Si, C, Cu, Fe, and Mn in the 1 ppmA and below region. The problem has been attacked in the following ways: (a) commercially available SSMS (in the United States); (b) localized-vibrational-mode absorption; (c) PL; (d) temperature-dependent Hall-effect measurements; and (e) photoconductivity (PC). Although the Hall-effect measurements can in certain cases give quite accurate quantitative results, nevertheless, the only well-established broadly applicable quantitative technique is SSMS. Accordingly about 50 samples have been analyzed at a cost of about \$8,000 and have compared the results with data from other experiments such as Hall mobility measurements (Reference 21). Furthermore, SSMS results have been compared from two different sources with each other, and have even had the same SSMS source run two different pieces of the same sample. The results of these investigations confirm that much of the SSMS data that has been received is not sufficiently accurate to permit meaningful comparisons with other data.

The other techniques mentioned above have at this state been established as good qualitative trace-analysis techniques for many important impurity elements. Several of the shallow acceptors, such as C, Cd, Zn, Mg, Si, and Be, for example, can be distinguished in PL (Reference 26). Likewise many of the deep impurities such as Cr and Fe (Reference 27) can be studied. The local vibrational mode technique has been used to identify trace amounts of Si, C, and Al in

our laboratory, and other elements have been identified in other laboratories. One added virtue of this technique is its ability to distinguish the lattice site of many of the impurity elements. Hall-effect and photoconductivity measurements have also been used to study and identify deep impurities, especially Cr and O. All of the techniques mentioned above could be made more quantitative if standards were established.

6. InP AND OTHER III-V COMPOUNDS

Although GaAs is certainly by far the most important III-V compound in terms of presently available devices, others such as InP and GaP also have wide-band-gap applications. In fact, in the last two years or so, the Department of Defense has funded a rather large amount of InP research in connection with high-frequency FET applications (Reference 28). Some of these samples have been characterized especially by Hall-effect, PL, and PC measurements. A new PC peak never seen before was found in the important substrate material, InP:Fe, and attributed to an intra-center Fe transition, in agreement with recent absorption measurements (Reference 29). A reasonable Fe concentration was calculated for the sample, but this result also must be checked against an established standard not yet existing.

Details of the results obtained from transport measurements are discussed in the following journal publications.

J. W. Farmer & D. C. Look, "Type Conversion in Electron-Irradiated GaAs", J. Appl. Phys. 50, 2970 (1979).

J. W. Farmer & D. C. Look, "Electron Irradiation Defects in n-type GaAs", Phys. Rev. (accepted).

D. C. Look, "Resonance Photoconductivity in Fe-doped InP", Sol. State Commun. (accepted).

D. C. Look, "Model for Fe^{2+} Intracenter-Induced Photoconductivity in InP:Fe", Phys. Rev. (accepted).

D. C. Look, "Infrared Spectral Detectivity of Cr-Doped GaAs," J. Appl. Phys. 49, 3543 (1978).

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B. K. Shin, D. C. Look, Y. S. Park, and J. E. Ehret, "Hall-Effect Measurements in Cd-Implanted GaAs," J. Appl. Phys. 47, 1574 (1976).

D. C. Look and J. C. Manthuruthil, "Electron and Hole Conductivity in CuInS_2 ," J. Phys. Chem. Solids 37, 173 (1976).

D. C. Look, "Mixed Conduction in GaAs:Cr," J. Phys. Chem. Solids 36, 1311 (1975).

SECTION IV

DEEP CENTER PHOTOLUMINESCENCE AND LATTICE DYNAMICS

A photoluminescence apparatus was established for studying deep centers where the optical transition is generally broader and amenable to investigation at lower optical resolution. A krypton laser is used as the exciting source and a cooled P_bS cell serves as the detector. This system has a variable temperature capability (4.2 - 400°K) which makes possible a greater understanding of the particular center being studied. The important Cr and O lines in GaAs have been well established but need to be correlated more thoroughly with data from other characterization techniques such as spark source mass spectroscopy. One important finding has been that Cr from a GaAs:Cr substrate can diffuse great distances at vapor phase epitaxy growth temperatures, even appearing on the surface of a 100 μ m thick epilayer. This phenomenon has important consequences in the growth of high purity buffer layers as well as doped epilayers.

The far infrared optical capability has contributed much to the characterization program. This apparatus uses large optics (7 inch x 9 inch gratings) to increase the light intensity with moderately good resolution (200 \AA /mm with a 1mm slit width at 30 μ m). The apparatus can be used to measure absorption emission and photoconductivity. Studies of restrahlen and local mode vibrations are important in materials characterization. Localized Vibrational Mode (LVM) spectroscopy is a very useful tool to investigate the behavior of impurities in semiconductors. When an impurity atom lighter in mass than that of Ga and As atoms is introduced in the GaAs lattice, it can either sit on the substitutional site or go in as an interstitial. If the impurity atom is located on the substitutional site it gives rise to a vibrational mode whose frequency is higher than the optical phonon frequency of the host lattice and can therefore be detected in the optical absorption above the restrahlen. Also, the introduction of the impurity atom breaks down the translational symmetry and therefore the vibrational mode is quite localized. The vibrational frequency of the interstitial impurity atom, however, can be either higher or lower than

the lattice optical phonon frequency depending upon the mass of the atom and its interaction with the surrounding atoms.

In GaAs one can introduce elements of Group II on Ga sites to obtain acceptors, elements of Group IV on both Ga and As sites to obtain donors and acceptors respectively, and elements of Group VI on As sites to get donors. In addition, one can have elements of Group III on Ga sites and elements of Group V on As sites to obtain isovalent impurities. As the vibrational frequency of the impurity atom depends upon its site location, LVM spectroscopy can be used to obtain this information. These modes are detected as absorption peaks in the transmission spectra in the far infrared, beginning at about 300 cm^{-1} . The positions of the peaks give the energies of the vibrational modes and the strengths of the peaks give information concerning the total number of such impurities.

We have studied local vibrational modes in GaAs doped with silicon up to concentrations of $10^{19} \text{ atoms/cm}^3$. We have observed absorption peaks due to silicon on Ga sites, silicon on As sites and due to silicon pairs located on nearest neighbor sites. We have also investigated the behavior of LVM due to carbon implanted in GaAs as a function of annealing temperature and have derived the fraction of carbon atoms on substitutional sites at various annealing temperatures. This was the first observation of the carbon local mode in ion implanted samples.

As a characterization technique, LVM spectroscopy has several advantages. It is non-destructive and gives information concerning the site location of the impurity atoms. It can detect both electrically active and inactive impurities.

The details of the results obtained from deep center photoluminescence and lattice dynamics are described in the following journal articles.

Paper published after May 1975

P. W. Yu

1. Effect of Oxygen in Photoluminescence from Chromium-doped Semi-insulating GaAs, Phil won Yu, accepted for the publication in Solid State Commun.
2. Deep Emission Centers in Ge-implanted GaAs, Phil won Yu, to be published in J. Appl. Phys. 1979 November Issue.
3. Electrical Measurements and Optical Activation Studies in Mg-implanted GaAs, Y. K. Yeo, Y. S. Park, and Phil won Yu, J. Appl. Phys. 50, 3274 (1979).
4. Photoluminescence in Mn-implanted GaAs - An Explanation on the 21.40-eV Emission, Phil won Yu and Y. S. Park, J. Appl. Phys. 50, 1097 (1979).
5. Comparison of Compensation Ratios Determined by Photoluminescence and Electrical Methods in Epitaxial GaAs, Phil won Yu, Solid State Commun. 27, 1421 (1978).
6. Excitation-dependent Emission in Mg-, Be-, Cd-, and Zn- implanted GaAs, Phil won Yu, J. Appl. Phys. 48, 5043 (1977).
7. Temperature Dependence of Photoluminescence from Mg-implanted GaAs, J. Appl. Phys. 48, 2434 (1977).
8. Photoluminescence from Mg-implanted GaAs, Phil won Yu and Y. S. Park, Appl. Phys. Lett. 30, 14 (1977).
9. Zn-ion-implantation Profiles in CuInSe₂ by Auger Electron Spectroscopy, Phil won Yu, J. T. Grant, Y. S. Park, and T. W. Haas, J. Appl. Phys. 48, 67 (1977).
10. Evidence for a Donor-Acceptor Pair Band in CuInSe₂, Phil won Yu, Solid State Commun. 18, 395 (1976).
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12. Radiative Recombination in Melt-grown and Cd-implanted CuInSe₂, Phil won Yu, J. Appl. Phys. 47, 677 (1976).
13. Electroluminescence and Photovoltaic Detection in Cd-implanted CuInSe₂ P-n Junction, Phil won Yu, Y. S. Park, S. P. Faile, and J. E. Ehret, Appl. Phys. Lett. 26, 717 (1975).
14. Observation of Localized Vibrational Mode Absorption of Carbon-Implanted GaAs and Effects of Annealing Temperature, M. M. Kreitman, T. W. Farmer, K. K. Bajaj, and C. W. Litton, Solid State Comm. 31,000, 1979.

SECTION V

AUTOMATED LUMINESCENCE TOPOGRAPHY SYSTEM

A new optical-scanning technique with a spatial resolution of $10\mu\text{m}$ has been developed for examining the spatial homogeneity of semiconductor wafers. The system consists of six basic components: 1) An Ar-ion laser for the exciting source, 2) a bidirectional scanner with focusing lens, 3) sample holder and helium Dewar for low-temperature analysis, 4) a spectrometer for high spectral resolution, 5) photomultiplier for photon counting, and 6) programmable calculator and interface package for experimental control and data processing.

In characterizing a material it is essential to know both the concentration and type of impurity present in the sample. Solid-state devices are fabricated on wafers which have been sliced from large boules of semiconductor device material. Since each wafer may contain hundreds of similar devices, it is important that the electrical properties of the material be homogeneous over the entire wafer. The scanning technique developed on this task provides a nondestructive analyses scheme for this type of uniformity characterization. Techniques such as Hall and mobility measurements lack both the necessary spatial resolution and nondestructive quality. A scheme has been developed for theoretically analyzing the experimental data to obtain both the donor and acceptor concentrations. These have been shown to agree very well with concentrations obtained from Hall measurements on the same sample.

Because of the automation and storage capabilities of the system, a number of different types of measurements can be made to characterize the material:

- 1) Varying λ , constant x , y - spectrum scan;
- 2) Constant λ , constant x (y), varying y (x) - one line topography;
- 3) Constant λ , varying x , y - full topography.

The first type of measurement provides a spectral scan at one specific spot on the wafer, the spot can be any x , y coordinate on the wafer. The second measurement can be made at any selected wavelength and displayed on the scope of the multichannel analyzer. This provides an analog

output of the luminescence variation along one of the axes. The third measurement can be made at a selected wavelength to provide a full topograph of the luminescence emitted from the sample.

The results of the topography experiments are described in the following journal articles:

- 1) Determination of Concentrations of Donors and Acceptors in GaAs by an Optical Method, S. B. Mann, D. W. Langer, D. L. Kingston, and M. J. Luciano, Appl. Phys. Letters, 31, 652 (1977).
- 2) Automated Luminescent Topographic System, M. J. Luciano and D. L. Kingston, Rev. Sci. Instrum. 49, 718 (1978)

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28. R. D. Fairman, M. Omori, and F. B. Yank, Ref. 2, p. 45.
29. G. W. Iseler (to be pub. in the Proc. of the Seventh Int. Symp. on GaAs and Related Compounds, St. Louis, 1978).